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Determination of the order of kinetics and activation energy in thermoluminescence peaks with temperature dependent frequency factor

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Abstract : A method to determine the order of kinetics and activation energy of thermoluminescence peaks with temperature-dependent frequency factor is presented. The method uses the peak temperature and/or the temperatures corresponding to the two points of inflection of the peak

Keywords : Thermoluminescence, order of kinetics, activation energy

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1. Introduction

Thermoluminescence (TL) glow peaks occur when the temperature of a previously excited crystal increases with time as a result of electron-hole recombination. The TL method is an important tool for the determination of the characteristics of electron trapping states in insulators and semiconductors. For the theoretical treatment of TL, normally it is assumed that frequency factor which is related to the electron capture cross section is independent of temperature. But due to the temperature dependence of type $T^{-\alpha}$ ($0 \leq \alpha \leq 4$) of electron capture cross sections [1–4], frequency factor will also depend on temperature as T^{u} ($-2 \leq u \leq 2$) [5,6]. Land [7] suggested a method of calculating trapping parameters from the inflection points and maximum of TL glow curves. Gartia *et al* [8] and Singh *et al* [9] put the method of Land [7] in a more usuable form by suggesting a number of expressions for the determination of the activation energy of TL peaks of arbitrary order of kinetics. But unlike Land [7], they did not consider the temperature dependence of frequency factor. In the present paper, the problem is reinvestigated by considering the temperature dependence of frequency factor.

2. Theory

Following Fleming [6], the glow intensity of a first order and non-first order TL glow peaks can be expressed respectively as

$$I(T) = Cn_0 s_0 T^a \exp\left[-E/(kT) - (s_0/\beta)\int_{T_0}^{T} T'^a \exp[-E/(kT')]dT'\right] \quad (1)$$

and

$$I(T) = Cn_0 s_0 T^a \exp[-E/(kT)]\left[1 + [s_0(b-1)/\beta] \times \int_{T_0}^{T} T'^a \exp[-E/(kT')]dT'\right]^{-b/(b-1)} \quad (2)$$

where the symbols have their usual meanings and for $b \neq 1$,

$$s_0 = s_0' n_0^{b-1}.$$

The temperature dependence of frequency factor is given by [5,6]

$$s = s_0 T^a. \quad (3)$$

The peak temperature T_m of the glow peak can be obtained from the relations

$$E/(kT_m^2) - s_0 T_m^a \exp\left(-E/(kT_m)\right)/\beta + a/T_m = 0, \quad (b=1) \quad (4)$$

and

$$a/T_m + E/(kT_m^2) = bs_0 T_m^a \exp\left[-E/(kT_m)\right]/\beta \times \left[1 + [s_0(b-1)/\beta] \int_{T_0}^{T_m} T'^a \exp[-E/(kT')]dT'\right]^{-1}, \quad (b \neq 1). \quad (5)$$

The integral $\int_{T_1}^{T_2} T'^a \exp[-E/(kT')]dT'$ appearing in eqs. (1), (2) and (5) cannot be solved analytically and therefore has been developed as

$$\int_{T_1}^{T_2} T^a \exp[-E/(kT)]dT = \left[\int_0^{T_2} T^a \exp[-E/(kT)]dT - \int_0^{T_1} T^a \exp[-E/(kT)]dT\right]$$

$$= (E/k)^{a+1}\left[\int_{u_2}^{\infty} u^{-a-2}e^{-u}du - \int_{u_1}^{\infty} u^{-a-2}e^{-u}du\right]$$

$$= (E/k)^{a+1}\left[\Gamma(-a-1,u_2) - \Gamma(-a-1,u_1)\right] \quad (6)$$

with $u = E/(kT)$. $\Gamma(a,x)$ is the incomplete complementary Gamma function [10]. The integral can now be evaluated numerically by using algorithm of Lentz on continued fraction [11]. This method converges rapidly and permits a very high precision.

Eliminating s_0/β from eqs. (1) and (4), one can write [12]

$$I / I_m = (u_m / u)^a \exp\left[u_m - u + F(u,u_m)\right] \quad (b = 1). \tag{7}$$

Similarly, eliminating s_0/β from eqs. (2) and (5), one gets

$$I / I_m = (u_m / u)^a \exp(u_m - u)\left[1 - [(b-1)/b]F(u,u_m)\right]^{-b/(b-1)}, (b \neq 1) \tag{8}$$

with $$F(u,u_m) = (au_m + u_m^2)u_m^a \exp(u_m)\left[\Gamma(-a-1,u_m) - \Gamma(-a-1,u)\right] \tag{9}$$

and I_m is the peak intensity.

The inflection points T_{i1} and T_{i2} in the rising and falling sides of a TL peak satisfy the equation.

$$\left(d^2I / dT^2\right) = 0 \qquad \text{for } T = T_{ij}\ (j = 1, 2). \tag{10}$$

Eq. (10) can also be written as

$$2(dI / du) + u(d^2I / du^2) = 0 \tag{11}$$

with $$dI / du = I(dF / du - a / u - 1), \quad (b = 1) \tag{12}$$

$$= -I(a / u + 1) + (u_m / u)^a \exp(u_m - u)(dG / du), \quad (b \neq 1) \tag{13}$$

$$d^2I / du^2 = I(d^2F / du^2 + a / u^2) + (dI / du)(dF / du - a / u - 1), \quad (b = 1) \tag{14}$$

$$= -(dI / du)(a / u + 1) + aI / u^2 + (u_m / u)^a \exp(u_m - u) \quad (b \neq 1)$$

$$\times\left[(d^2G / du^2) - (dG / du)(a / u + 1)\right], \tag{15}$$

where $$G = D^{-b/(b-1)}, \tag{16}$$

$$D = 1 - \left((b-1)/b\right)F(u,u_m). \tag{17}$$

For the case of temperature-independent frequency factor ($a = 0$), the eqs. (12)–(17) reduce to corresponding expressions of Gartia *et al* [8].

Eq. (11) has been solved by using Newton-Raphson method [11]. To a good approximation, a plot of $u_{i1} / (u_{i1} - u_m)$, $u_{i2} / (u_m - u_{i2})$ and $u_{i1}u_{i2} / [u_m(u_{i1} - u_{i2})]$ against u_m are found to be linear. The linear relationship is illustrated in Figure 1 for the pair $u_{i1}/(u_{i1} - u_m)$ and u_m for $b = 2$ and $a = 2$.

Hence, one can write

$$u_m = A_1u_{i1} / (u_{i1} - u_m) + B_1, \tag{18}$$

$$u_m = A_2u_{i2} / (u_m - u_{i2}) + B_2, \tag{19}$$

$$u_m = A_3u_{i1}u_{i2} / [u_m(u_{i1} - u_{i2})] + B_3, \tag{20}$$

where $u_{i1} = E/(kT_{i1})$ and $u_{i2} = E/(kT_{i2})$.

Eqs. (18)–(20) can also be written as

$$E_1 = A_1 kT_m^2 / (T_m - T_{i1}) + B_1 kT_m, \tag{21}$$

$$E_2 = A_2 kT_m^2 / (T_{i2} - T_m) + B_2 kT_m, \tag{22}$$

$$E_3 = A_3 kT_m^2 / (T_{i2} - T_{i1}) + B_3 kT_m. \tag{23}$$

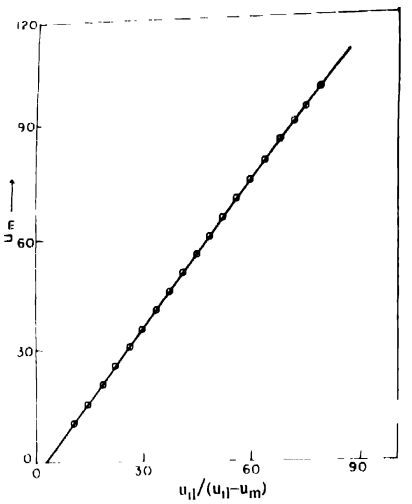

Figure 1. Linear plot of u_m against $u_{i1}/(u_{i1} - u_m)$ for $b = 2$, $a = 2$

The coefficients A_j and B_j ($j = 1, 2, 3$) occurring in eqs. (18–23), are calculated for different values of $a(2<a<-2)$ for a particular value of b. The method of linear least squares [13] has been used to express each of the coefficients A_j and B_j as a linear function of a as

$$A_j = C_{0j} + C_{1j}a, \tag{24}$$

$$B_j = D_{0j} + D_{1j}a. \tag{25}$$

The coefficients $C_{0j}, C_{1j}, D_{0j}, D_{1j}$ ($j = 1, 2, 3$) occurring in eqs. (24)–(25), are determined by solving the normal eqs. [13] for the least square lines (24) and (25) and are presented in Table 1.

Table 1. Co-efficient C_{0j}, C_{1j}, D_{0j} and D_{1j} occurring in equations (24) and (25)

b	j	C_{0j}	C_{1j}	D_{0j}	D_{1j}
1.0	1	0.9627	−0.0003	−0.5617	−0.9759
	2	0.9626	−0.0003	−0.6980	−0.9753
	3	1.9253	−0.0005	−0.6294	−0.9755
1.5	1	1.5866	−0.0005	−1.1746	−0.9602
	2	1.1585	−0.0005	−1.1436	−0.9546
	3	2.3172	−0.0010	−1.3043	−0.9575
2.0	1	1.3159	−0.0007	−1.7181	−0.9477
	2	1.3156	−0.0008	−2.0967	−0.9398
	3	2.6314	−0.0014	−1.9053	−0.9440

3. Results and discussions

The points of inflection of numerically computed TL peaks have been evaluated by solving eq. (11) with Newton-Raphson method [11]. The computer code has been checked

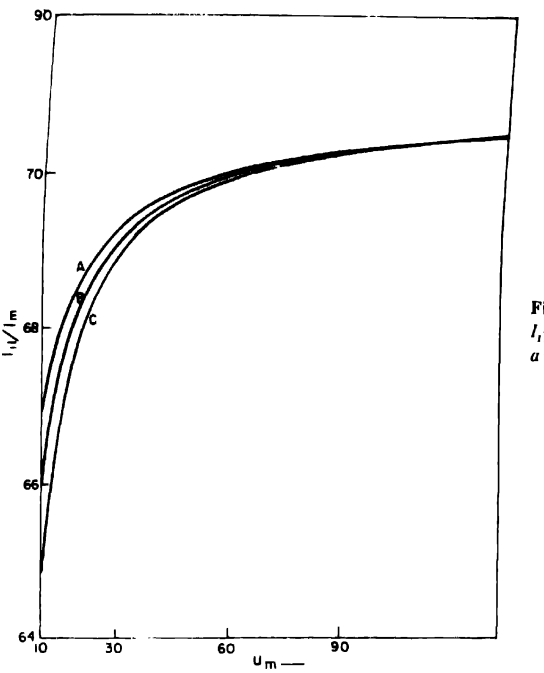

Figure 2. Fractional intensity I_{11}/I_m against u_m for b = 1, A $a = 2$, B $a = 0$ and C $a = -2$.

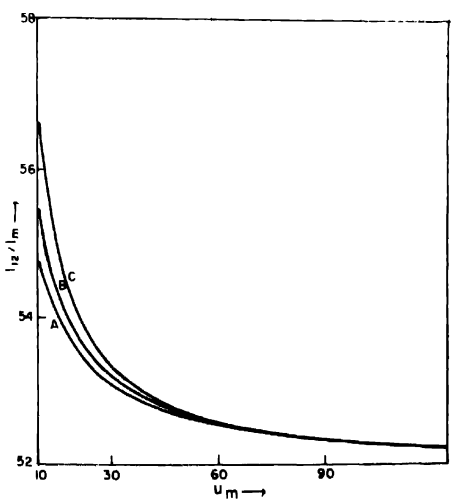

Figure 3. Same as in Figure 2 but for the second point of inflection

by reproducing the results of Land [7] and Gartia *et al* [8] (Table 2). In Figures 2 and 3, the fractional intensities I_{1j}/I_m (j = 1, 2) at the two points of inflection for first order kinetics

Table 2. Activation energies (in ev) of numerically generated peaks reported (E_{in}) by Land [7] and Garlia *et al* [8] by using present set of formulas and Land [7] formula. E_1, E_2, E_3 correspond to the present set of formulas and E_{1L}, E_{2L} denote the activation energies calculated byusing Land [7] formula. $E(a = 0)$ denote the energies calculated by setting $a = 0$

b	E_{in} (eV)	T_m (K)	a	T_{t1} (K)	T_{t2} (K)	E_1 (eV)	E_2 (eV)	E_3 (eV)	E_1(eV)	E_2(eV)	E_3(eV)	E_{1L} (eV)	E_{2L} (eV)
									$a = 0$				
1 0	0 20	97 2	0	93 4	101 0	0 2000	0 2000	0 2000				0.2000	0.2000
1 0	0 20	97 2	2	93 7	100 7	0 2000	0.2000	0.2000	0.2165	0.2165	0 2165	—	—
1 0	0 67	311 0	0	299.3	322 7	0 6699	0 6700	0.6700				0.6700	0.6700
1 0	0 67	311 0	2	300 1	321 8	0.6701	0 6701	0 6701	0 7229	0 7229	0 7229	—	—
1 0	1 2	545 2	0	525 1	565.2	1 2000	1 2000	1 1999				1 2000	1 2000
1 0	1 2	545 2	2	526 5	563.8	1 2001	1 2002	1 2002	1.2927	1 2927	1.2927	—	—
2 0	0 2	96 9	0	91 9	101 8	0 2001	0.2001	0.2001				0 2000	0 1998
2 0	0 2	96 9	2	92.3	101 5	0 2001	0 2001	0 2001	0.2162	0 2161	0.2162	—	—
2 0	0.67	310 2	0	295 0	325 2	0 6702	0 6703	0.6703				0 6699	0 6700
2 0	0 67	310.2	2	296.0	324 2	0.6704	0 6704	0 6704	0 7220	0 7218	0.7219	—	—
2 0	1 2	543.9	0	517 7	569 7	1 2004	1 2006	1 2005				1 2000	1.1993
2 0	1 2	543 9	2	519 4	568 0	1.2008	1.2009	1 2008	1.2913	1 2909	1 2911	—	—
1 0	1 0	536 5	0	513 2	559 6	1 0000	1 0000	1 0000				1 0000	1 0000
1 0	1 0	488 7	0	469 3	507 9	0 9999	1 0000	0 9999				1 0000	1.0000
1 0	1.0	448.4	0	432 1	464 7	1 0000	1 0000	0.9999				1 0000	1 0000
1 0	1 0	414.1	0	400 2	428 0	1 0000	1 0000	0.9999				1 0000	1 0000
1 0	1 0	384 6	0	372 5	396 6	1 0000	0 9999	0 9999				1.0000	1 0000
1 5	1 0	535 6	0	508 4	562 4	1 0001	1 0001	1 0001				—	—
1 5	1 0	488 0	0	465 3	510.4	1 0001	1 0001	1 0001				—	—
1 5	1 0	447 9	0	428 7	466.9	1 0001	1.0002	1 0001				—	—
1 5	1.0	413 7	0	397 3	430.0	1.0001	1 0001	1.0001				—	—
1 5	1 0	384 2	0	370 0	398 2	1 0001	1 0002	1 0002				—	—
2.0	1 0	534.7	0	504.7	564.3	1.0002	1.0002	1 0002				1 0000	0.9988
2 0	1 0	487 3	0	462 2	512.1	1 0003	1 0004	1.0003				0 9988	0.9992
2 0	1 0	447 4	0	426.1	468.4	1.0004	1 0005	1.0004				0.9999	0.9994
2 0	1 0	413 3	0	395 0	431 3	1 0004	1 0005	1 0005				0 9999	0 9996
2 0	1 0	383 9	0	368 1	399 5	1 0004	1 0006	1 0005				0 9999	0.9997

($b = 1$) corresponding to $a = -2$, 0 and 2 are plotted against u_m. The results for other values of a fall between the curves for $a = -2$ and $a = 2$ and cannot be distinguished in the present scale of the figure. From Figure 2, it is seen that the fractional intensity corresponding to the first point of inflection increases with u_m but for $u_m \geq 40$, it does not change much. On the other hand, the fractional intensity corresponding to the second point of inflection decreases with increasing u_m. But like the first point of inflection, this ratio is almost insensitive to u_m and a for $u_m \geq 40$. The same feature is observed for second order kinetics

($b = 2$) (Figures 4 and 5). In Figure 6, the variation of the fractional intensities as a function of the order of kinetics (b) is given for $u_m = 40$ and for $a = -2, 2$. It is to be noted that the

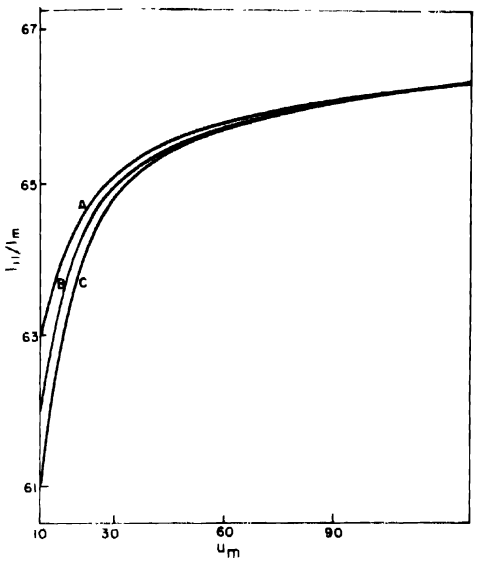

Figure 4. Same as in Figure 2 but for $b = 2$

inflection point in the falling side of the peak is more sensitive to the order of kinetics than that corresponding to the rising side. Figure 6 can be used for the preliminary estimation of the order of kinetics like the curve connecting μ_x and b [5].

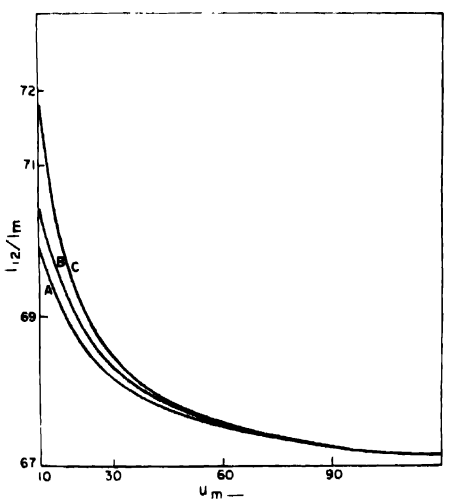

Figure 5. Same as in Figure 3 but for $b = 2$

Now the determination of the activation energy is considered. As already noted, the coefficients occurring in eqs. (21)–(23) for the evaluation of the activation energy depend

on b and a. In Table 2, the activation energies of some numerically computed TL peaks reported by Land [7] and Gartia *et al* [8] are presented. If the temperature dependence of frequency factor with $a = 2$ is considered, there is a change in the values of T_{i1} and T_{i2}.

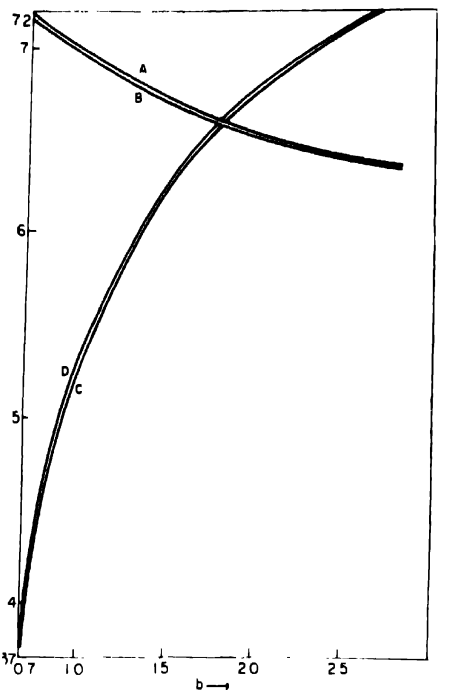

Figure 6. Variation of fractional intensities at two points of inflection against order of kinetics (b). A, B, C, D stand respectively for I_{i1}/I_m ($a = 2$), I_{i1}/I_m ($a = -2$), I_{i2}/I_m ($a = 2$) and I_{i2}/I_m ($a = -2$)

It is found that there is an excellent agreement between the input values of energy (E_{in}) and the energies E_j ($j = 1, 2, 3$) calculated by using the present set of expressions (21)–(23) when the actual values of a are used. But the difference in the values of T_{i1} and T_{i2} with $a = 2$, results in an error of activation energy by 7% to 8% if eqs. (23)–(25) are used with $a = 0$ rather than with $a = 2$. The activation energies of TL peaks (with $a \neq 0$) calculated by setting $a = 0$ are denoted by E_j ($a = 0$). But as already noted, the inflection points are not much sensitive to the values of a in accordance with the observations of Fleming [6]. As a result, it is very difficult to determine a. To estimate the error for a wide range of u_m ($10 \leq u_m \leq 100$) in the determination of activation energy due to the lack of information about the value of a, the formulae of activation energy for $a = 0$ are used to determine the activation energies of some numerically computed TL peaks with $a \neq 0$ and in Figure 7, the proportional percentile error $\delta = [|E_{in} - E_c|/E_{in}] \times 100\%$ is plotted as a function of $u_m = E/(kT)$ for $b = 2$ and $a = -2, 2$ (E_{in} is the input value of the activation energy and E_c is the calculated value of the activation energy for $b = 2$ by using the formula involving both the inflection points). The values of E_{in} and T_m to obtain E_c are choosen such that E_{in} and u_m lies in the ranges 0.5 eV $\leq E_{in} \leq$ 2.0 eV and $10 \leq u_m \leq 100$. It is seen that the activation

energy is over-estimated for the case of $a = 2$ and under-estimated for $a = -2$. δ decreases from about 9.5% to about 3% as u_m changes from 20 to 80. The same feature is observed for other values of b. So, it is observed that the temperature dependence of frequency factor can lead to a maximum error of around 10% in the determination of activation energy by point of inflection method.

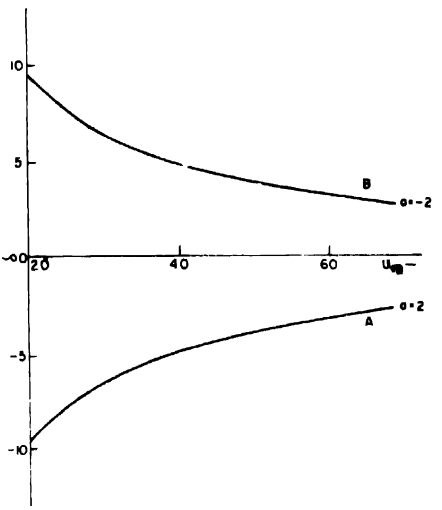

Figure 7. Plot of proportional percentile error δ against u_m for $b = 2$ A $a = 2$ and B $a = -2$

In Table 2, calculation of activation energies of the numerically generated TL peaks of Land [7] and Gartia *et al* [8] has also been done using the formulae presented by Land [7]. Gartia *et al* [8] commented that the formulae of Land do not work well. But it is observed that in order to obtain accurate results by using Land's formula, one has to carry on iteration. In the present work, the iteration has been carried out using Newton-Raphson method [11]. For $b = 1$, rapid convergence is obtained but for $b = 2$, a large number of iterations is required. The present set of formulae are superior to those of Land in the sense that no iteration is required and can be used for any value of b. The formulae of Land [7] are available only for $b = 1, 2$ and for $a = 0$.

Finally, the applicability of the method is considered by taking well-studied experimental 165.5°C TL peaks of Ca-doped KCl [14] and 320°C bluish green michroline (K Al Si_3O_8) [15]. It has been shown by Singh *et al* [9] that these peaks correspond to $a = 0$. Using Figure 6, it is found that these peaks obey first and second-order kinetics respectively. But since the determination of a for an experimental TL peak in accordance with Fleming [6] is difficult, the possible shift in the determination of the activation energies with different values of a ($-2 \leq a \leq -2$) is presented in Table 3. The values of E_j ($j = 1, 2, 3$) using the present set of expressions (21)–(23) and the values of $a = -2, -1, 0, 1, 2$ but using the same observed values of T_{t1} and T_{t2} for all values of a are presented in Table 3. From Table 3, it is seen that the activation energies are over-estimated for the case

of $a < 0$ and under-estimated for $a > 0$ which is opposite to the observations in Figure 7 and Table 2 where there is over-estimation for $a > 0$ and under-estimation for $a < 0$. This is due to the fact that while observing the shifts in energies in Figure 7 and Table 2, the shifted values of the inflection points with a are used to calculate E by setting $a = 0$; but in Table 3, the shifts in energies are calculated using the same observed values of the inflection points

Table 3. Activation energies E_j (j = 1, 2, 3) of some experimental peaks [9,14,15] computed with the observed values of T_{j1} and T_{j2} and by using present set of expressions setting at values of a = -2, -1, 0, 1, 2

T_m(eV)	β(K s^{-1})	T_m(K)	T_{j1}(K)	T_{j2}(K)	b	a	E_1(eV)	E_2(eV)	E_3(eV)
1.36	0.4167	438.5	426.9491	450.0051	1	-2	1.4342	1.4343	1.4342
1.36	0.4167	438.5	426.9491	450.0051	1	-1	1.3970	1.3971	1.3971
1.36	0.4167	438.5	426.9491	450.0051	1	0	1.3598	1.3599	1.3599
1.36	0.4167	438.5	426.9491	450.0051	1	1	1.3225	1.3227	1.3226
1.36	0.4167	438.5	426.9491	450.0051	1	2	1.2852	1.2854	1.2853
1.42	0.6667	593.0	566.562	619.0944	2	-2	1.5186	1.5182	1.5071
1.42	0.6667	593.0	566.562	619.0944	2	-1	1.4697	1.4695	1.4696
1.42	0.6667	593.0	566.562	619.0944	2	0	1.4206	1.4208	1.4207
1.42	0.6667	593.0	566.562	619.0944	2	1	1.3713	1.3717	1.3715
1.42	0.6667	593.0	566.562	619.0944	2	2	1.3219	1.3226	1.3222

but using the expressions (21)–(23) setting at different values of a. But in both the cases, the maximum error lies within 10%. The possible theoretical shifts in the values of T_{j1} and T_{j2} for these experimental peaks with different values of a ($-2 \le a \le 2$), have also been calculated and are found to show a marginal change around 1%.

4. Conclusion

In this paper, the point of inflection method for the determination of the activation energy of a TL peak suggested by Land [7] and refined by Gartia *et al* [8] and Singh *et al* [9] has been generalised for the case of temperature-dependent frequency factor. The present sets of expressions unlike those of Land [7], do not require any iteration and can be directly used. It is also found that in accordance with the findings of Fleming [6], it is difficult to distinguish TL peaks corresponding to different values of a.

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